

Matching rules from Al-Co potentials in an almost realistic model

Sejoon Lim,^{*} Marek Mihalkovič,[†] and Christopher L. Henley
Dept. Physics, Cornell University, Ithaca, New York, 14853-2501

We consider a model decagonal quasicrystal of composition $\text{Al}_{80.1}\text{Co}_{19.9}$ – closely related to actual structures, and using realistic pair potentials – on a quasilattice of candidate sites. Its ground state, according to simulations, is a Hexagon-Boat-Star tiling satisfying Penrose’s matching rules. In this note, we rationalize these results in terms of the potentials; the Al-Co second-neighbor potential well is crucial.

From the discovery of quasicrystals, it has been difficult to decide whether they are stabilized by entropy or by energy. (Here “energy” means an ideally quasiperiodic ground state.) In the decagonal case, the fastest route to a resolution may be ab-initio-based modeling. Recently, we observed a ground state [1] that perfectly implements Penrose’s matching rules [2] in a toy model of a binary Al-Co quasicrystal, closely related to realistic d(AlNiCo) models [3, 4, 5]. In this contribution, we sketch the matching rules’ origin; in particular, how fine-tuned must the potentials be to obtain this result?

Our simulations use a recipe introduced to study real Al-Co-Ni phases [3, 4, 5]. The only input data are the number density, the composition ratio, and the (quasi)lattice constants (tile edge is $a_R \equiv 2.455 \text{ \AA}$ and layer spacing $c/2 \equiv 2.04 \text{ \AA}$). In an initial “unconstrained” Monte Carlo simulation the atoms hop as a lattice gas on discrete, properly placed candidate sites (see [3, 4]), which decorate random rhombus tilings (that are rearranged as another kind of Monte Carlo move). The *lowest* energy configuration visited during the run is saved (which is far better than a typical state, due to energy fluctuations in these relatively small systems). The second stage is a “constrained” simulation flipping HBS tiles with a fixed atomic decoration (which allows larger systems) inferred from the unconstrained results.

The result (Fig. 1) is a Hexagon-Boat-Star (HBS) tiling of edge 2.45 \AA with Al atoms at exterior vertices and Co atoms on the interior rhombus vertex, as well as (respectively) one, two, or two internal Al atoms. Importantly, an Al vertex site goes vacant if it would have no Co nearest neighbors. For the present work, we introduced a “half-constrained” simulation in which atoms hop as a lattice gas on HBS tiles, limited to a site list of the ideal vertex sites, plus sites $1/\tau^2$ out along the midline of each Fat rhombus. This revealed that rearrangements are induced next to the empty vertices, such that the ground state is not literally the Penrose tiling (e.g. the defect marked by a pair of V’s in Fig. 1.) However, we believe quasiperiodicity is maintained (the shape of hyperatoms in 5D space will change slightly).

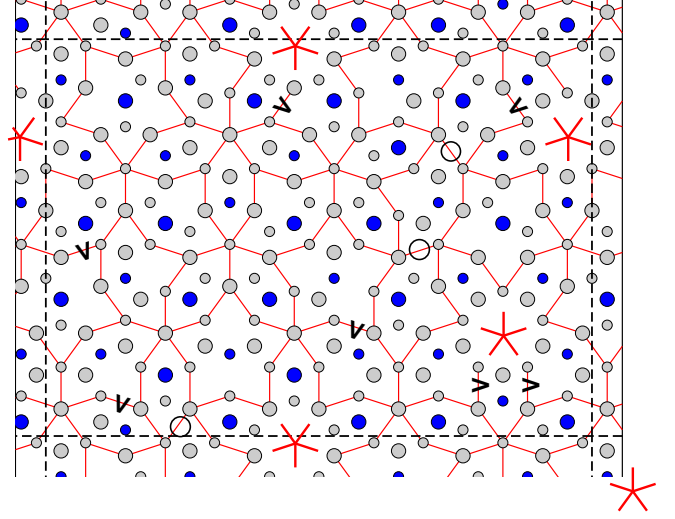


FIG. 1: Best unconstrained configuration from original discovery runs, placing atom content $\text{Al}_{169}\text{Co}_{42}$ in a smallish cell $31.9 \times 23.3 \text{ \AA}$, with periodic boundary conditions. We cooled gradually to $T \approx 1100\text{K}$ with 10^5 trial atom swaps per swappable pair, and 2000 tile flips per flippable pair during the run. Co and Al atoms are shown by black and gray circles; large/small circles indicate the top/bottom layers. The seven V-rule violations (i.e. fat rhombus/thin rhombus) are marked “V”, the three fat/fat violations are marked with circles, and the three vacated Al sites are marked by asterisks. Four violations are necessitated by periodic boundary condition. The pair of V’s in the lower right corner mark an energetically favored defect (see text).

I. ORDERING AND DIAGNOSTICS

The interactions (we used “GPT” potentials [3, 6]) have the following properties: (i) $V_{\text{AlAl}}(R)$ has a strong hard-core repulsion at close neighbor distances ($R < 2.8 \text{ \AA}$). (ii) $V_{\text{AlCo}}(R)$ is extremely attractive at $R \approx 2.5 \text{ \AA}$; (iii) $V_{\text{CoCo}}(R)$ has a rather strong attraction at the second-neighbor distance $R \approx 4.5 \text{ \AA}$, due to the prominent Friedel oscillations; (iv) similarly $V_{\text{AlCo}}(R)$ is attractive, too, around $R \approx 4.5 \text{ \AA}$; this well is mainly responsible for the matching rules [1].

How does this order follow from these potentials? The question falls into two parts. (i) Why the HBS tiling? (ii) Granted the atoms do form an HBS tiling, why do the interactions force matching rules? This is the focus of Sec. II, which uses inflated (edge 4 \AA) HBS tiles to examine the energies with more detail than Ref. [1].

In Ref. [1] we identified four aspects of ordering, the first

^{*}Current address: 311-602 Hyundai Apt.; Bora-dong, Giheung, Yongin; Gyeonggi-do, South Korea 446582

[†]Also Institute of Physics, Slovak Academy of Sciences, Dubravská cesta 9, 84511 Bratislava, Slovakia (permanent address).

TABLE I: Important bond distances and potential values, bonds of each kind $N(R)$ per cell, and change $\Delta E_{a,b}^R$ in the contribution to the total energy change $E(T_b) - E(T_a)$, per cell. (Interlayer distances are written R_2 .) The same cell and atom composition were used as in Fig. 1; temperatures were $T_\infty \approx 5000\text{K}$, $T_1 \approx 2000\text{K}$ (using a randomly chosen typical configuration after equilibration, from the “half-constrained” simulation); T_0 refers to the near ground state, the best found during a run at low temperature.

R (Å)	pair (AB)	$V_{AB}(R)$ (eV)	$N(R)$	$-\Delta E_{0,1}$ (eV/cell)	$-\Delta E_{0,\infty}$ (eV/cell)
2.455	Al-Al	0.4124	119	+0.8247	+5.7729
	Al-Co	-0.2919	152	-0.5839	+1.4597
2.542	Al-Al	0.2758	248	-1.1033	-3.8615
	Al-Co	-0.2583	240	+2.0661	+1.0331
	Co-Co	0.1001	0	0.0000	+0.2002
2.886	Al-Al	0.0791	170	-0.7119	-0.7119
	Al-Co	-0.0427	52	+0.0427	+0.3416
	Co-Co	0.0950	0	+0.0000	+0.3801
3.016	Al-Al	0.0669	0	+0.0669	+0.0000
3.192	Al-Al	0.0637	274	+0.6373	+1.5296
	Al-Co	0.0913	0	+0.9127	+0.0000
3.789	Al-Al	0.0264	126	-0.0528	-0.5281
	Al-Co	0.0554	2	+0.5538	+1.4953
3.846	Al-Al	0.0212	126	+0.6375	+0.3825
	Al-Co	0.0424	0	+0.0848	+1.2722
4.303	Al-Al	-0.0055	144	-0.0439	-0.0439
4.465	Al-Al	-0.0071	456	+0.3811	+0.4940
	Al-Co	-0.0349	528	+1.3261	+1.3959
	Co-Co	-0.0909	116	-0.5453	+1.2724
4.669	Al-Al	-0.0049	283	+0.0147	-0.0978
	Al-Co	-0.0260	149	+0.0521	+0.8337
	Co-Co	-0.0796	45	+0.3183	-0.1591
4.762	Al-Al	-0.0028	247	-0.1039	-0.2254
	Al-Co	-0.0189	304	-0.0756	+0.1702
4.997	Al-Al	0.0015	340	-0.0278	-0.0278
	Al-Co	0.0012	104	-0.0023	-0.0187
	Co-Co	-0.0193	0	0.0000	-0.1543

two of which develop at relatively high temperatures ($T \geq T_1 \equiv 1000\text{ K}$). Aspect (1) is formation of the 2.45-Å HBS tiling, with Co in the center and Al decorating the corners of every tile, as is quite universal in Al-transition metal decagons. HBS tiles trivially satisfy the Penrose *double* arrows. The HBS formation is attributed to the nearest-neighbor Al-Al and Al-Co interactions [1]. Medium-temperature configurations from an “unconstrained” simulation may have many defects (of matching rules, or placement of Al atoms internal to the HBS tiles), but the HBS framework itself is inviolate.

Aspect (2) is the Co-Co network due to second-neighbor Co-Co attraction: a supertiling of inflated HBS tiles (edge $\tau a_R \approx 4\text{ Å}$) and small generalizations (e.g. pillow tile, below). But at medium T , the Co-Co tiling is not yet a Penrose inflation of the 2.45Å-level HBS tiling.

The other two aspects of order appear at $T < T_1$ and implement matching rules. Aspect (3) is the “V-rule”: a convex ($2\pi/5$) corner of the Thin rhombus in the (2.45Å) H or B tile can only adjoin a concave ($3\pi/5$) corner of the B or S tile, and vice versa. This ties together the HBS tiling and the Co supertiling, requiring that every Co-Co edge have a Fat Hexagon around it. The V-rule is simply the Penrose (single-arrow)

matching rule between Fat and Thin rhombi, as it is manifested on our (small) HBS tiles. Aspect (4) of the ordering – the final stage – is to satisfy Penrose single arrows between two Fat rhombi, on the edges not involved in the V-rule (two on every Hexagon and Boat); its explanation is deferred to Sec. II.

Of course, the V-rule demands an equal number of the respective kinds of corner, thus $n_V = 2n_H + n_B = 2n_B + 5n_S$. Combined with the formula for the numbers of rhombi, $n_H + 3n_B + 5n_S = n_{\text{fat}}$ and $2n_H + n_B = n_{\text{thin}}$, this completely specifies the number of H, B, and S tiles. In the limit of zero phason strain, we get densities (n_H, n_B, n_S) = $(\tau^{-4}, \tau^{-5}, \tau^{-5}/\sqrt{5})$ (per rhombus) exactly as in the Penrose tiling. (Also, if matching rules are obeyed, the vacated Al sites are centers of inflated Star tiles and their density is $n_{\text{vac}} = \tau^{-7}/\sqrt{5}$, which gives the $\text{Al}_{80.1}\text{Co}_{19.9}$ stoichiometry, and the point density of $0.0697/\text{Å}^3$.)

There were two key diagnostics for our initial identification of the key interactions for matching rules. First, we compared the contributions of each pair distance R to the total energy as a function of temperature (Table I). As evidence for the story just given, big changes are seen upon cooling $T_\infty \rightarrow T_1$, but none from T_1 downwards, in (i) nearest neighbor [2.45–2.86Å] Al-Al and Al-Co, forming HBS tiles, and (ii) in Co-Co 4.47–4.67Å, forming the Co-Co network. The big changes at lower T were in Al-Co at 3.79–4.67Å, in accord with the analysis of Sec. II (below).

The second diagnostic was to vary the potential cutoff radius r_{cut} (which was usually 7 Å). At $r_{\text{cut}} = 5.1\text{ Å}$ the Penrose rules are still satisfied whereas at $r_{\text{cut}} \approx 3.5\text{ Å}$ one gets an HBS tiling but no matching rules, confirming independently that HBS formation is due to nearest-neighbor bonds but matching rules come from second-neighbor bonds. Furthermore, if $r_{\text{cut}} = 5.1\text{ Å}$ and internal Al’s are removed from all tiles, [10] the tiling implements the V-rule but not the Fat-Fat rule, confirming the role assigned in Sec. II to the “b” atoms in Fig. 2 and similar Al.

II. MATCHING RULES VIA 4.0 Å TILING

Aspect (4) of the ordering – the final stage – is to satisfy Penrose arrows on the remaining Fat rhombus edges (two on every Hexagon and Boat). Let’s focus now on the Fat rhombus/Fat rhombus matching rule, the crucial aspect (4) of the ordering process. To check the energy cost of a Fat/Fat violation, which depends on the internal Al in those Fat rhombi, We reformulate the matching-rule problem in terms of the 4.0Å *supertiles*, in which arrows are defined on every edge by the Al atom position. A given supertiling can be broken into HBS tiles in several ways, corresponding to different arrowings of its edges. Note that usually (as in our 2.45Å-HBS tiling), the degrees of freedom are in the tiles, and possible mismatches occur along tile-tile edges; whereas in the 4.0Å-HBS model, each edge is an independent degree of freedom, and the possible mismatches occur between two edges in the same tile. (The same was true for the near-matching-rule of $d(\text{AlCuCo})$ [7].)

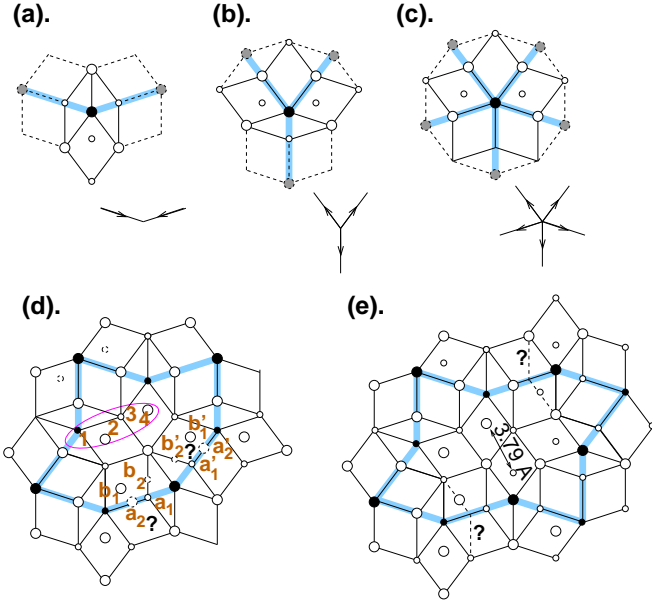


FIG. 2: Inflated edges (broad shaded lines), as forced by the “V-rule”. Solid lines show (a) H, (b) B, and (c) S tile; dashed lines are fragments forced by the V-rule. Insets below show the arrow decorations at the inflated scale (d). The arrowings of edges marked “?” are undetermined by the V-rule. Interactions between the labeled atom sites determine the Penrose arrowing as optimal. (e). Besides H, B, and S, only this pillow tile is consistent with the “V-rule”, but it forces the unfavorable Al-Al distance of 3.79\AA .

The Co-Co network has 4.46\AA bonds, along supertile edges, and 4.67\AA bonds. All of the latter relate endpoints of a $2\pi/5$ supertile corner (e.g. in Fig. 2(c)). Assuming the V-rule, [see Fig. 2(a,b,c)], that makes five bonds per (small) B and five per small S tile. Hence, if the H-B-S content is fixed (as implied by the V-rule), the number of 4.67\AA Co-Co bonds is fixed and they do not contribute to the matching rule. (That same number, in the super tiling, is 2 per H, 3 per B, and 5 per S tile, so the super HBS content is also constrained.)

What supertiles are possible? A corollary of the V-rule is that, at any $(2\pi/5)$ [resp. $3(2\pi/5)$] corner, both arrows point out from [resp. into] the corner. The other constraint is that no interior space be left after a supertile’s border is decorated by HBS tiles (filling an interior always violates the V-rule). The conclusion is we can have the super-H, B, and S tiles, or the “pillow” tile shown in Fig. 2(e) (or extensions of it by adding more segments of alternating $2(2\pi/5)$ and $3(2\pi/5)$ corners.)

So let’s consider the super-Boat tile (Fig. 2) (d). The V-rule leaves undetermined whether the two edges marked “?” both point to the same corner (as shown) or are flipped with one in and one out (this version violates the Penrose rule). Depending on the choice for the first arrow, we either have Al at a_1 and b_1 , or else at a_2 and b_2 ; similarly the primed sites depend on the second arrow. The energy difference between the options for first arrow depends on 16 possible interactions between sites a_1 , b_1 , a_2 , b_2 and the fixed atoms marked 1,2,3,4. (Several other fixed atoms interact, but they are symmetrically placed relative to the flip, so they can’t affect the energy differ-

ence.) In addition, there are four interactions between (a_i, b_i) and (a'_i, b'_i) , however we must exclude those that connect two sites on the same tile. (That term was counted already in the energy per tile, and as noted earlier the total counts of H, B, and S tiles were fixed by the V-rule.)

Here are the biggest contributions (energies are in Table I): either option makes one Al-Co(4.67) bond; the “right” way also gets two Al-Co(4.47) – quite favorable – and one Al-Al(2.89) – very unfavorable; the “wrong” way gets four Al-Al(3.85) and two Al-Al(3.79) which are unfavorable. The “right” way also makes eight Al-Al(4.47) – favorable – versus just two for the “wrong” way. The net difference is 0.1825 eV in favor of the “right” way. Preliminary numerical tests, correlating total energy with the number of matching rule violations, indicate a typical matching-rule defect (of either kind) actually costs the order of 0.1 eV .

Next, consider the super Hexagon. Its side edge arrows are free to point either way, but a calculation like that for the Boat says these arrows are favored to be parallel, which is the proper Penrose arrowing of a Boat. Finally, the V-rule permits just one possible arrowing on the super-Pillow tile (Fig. 2), which forces a Fat-Fat rhombus violation in the middle associated with unfavorable Al-Al distances. Hence we expect this tile loses out to the super-Star (which carries the same count of 2.45\AA HBS tiles).

III. DISCUSSION

The matching rules are mostly implemented by Al-Co interaction at $\sim 3.8\text{\AA}$ and 4.46\AA ; however, they are a resultant of many terms, and the cost of a rule violation seems to be context-dependent (especially with our standard potential cut-off at 7\AA , which includes the third well.) Fortunately, as seen in the example of Sec. II, this isn’t a “frustrated” problem: most contributions have the same signs. We checked the cost E_{match} of a rule violation: a fit of total energy versus number of violations (counted by hand) in 10 low-energy configurations (from $T \approx 10^3\text{K}$) gave $E_{\text{match}} \approx 0.1\text{eV}$. If we took a (near) ground state and moved the violation along a “worm” by local HBS flips, however, the cost was $\sim 0.5\text{eV}$, suggesting the minimum four violations forced by periodic boundary conditions had found sites where their cost was anomalously low.

The matching rule depends on having the exact ratio of H:B:S tiles. That is a worry: by local flips, one can trade tiles $HS \rightarrow BB$ or vice versa. Let’s define energies E_H, E_B, E_S as the sum of interactions within each tile (including a chemical potential μ_{Al} , since a flip changes the number of Al atoms). Then one naively expects to maximize or minimize n_B , depending whether $E_H + E_S - 2E_B$ is positive or negative, which would prevent reaching the right composition. But the tile-tile (matching-rule) interactions create a “gap” in Al site energies so that running the reaction in *either* direction costs a positive energy.

The rule also depends on having the right internal Al decoration in every HBS tile. We studied the same model with Al-Ni: those potentials are quite similar to Al-Co (except the

Al-Ni attraction is not quite as strong as Al-Co). The Penrose tiling may well be the ground state for Al-Ni — indeed, the *constrained* simulation behaves the same for Al-Co and Al-Ni — but it was less robust in the *unconstrained* simulation: e.g., B tiles with just one internal Al on the mirror axis are metastable.

As a reality check, we note that according to pair potentials, the (relaxed) matching-rule structure is unstable by 69.9 meV/atom compared to the tie-line between Al_9Co_2 (19% Co) and other competing phases. [For this calculation we used the optimal “half-constrained” simulation result for the same size as Fig. 1.] The (relaxed) ab-initio energy, using the VASP package [8], came out unstable by 98.5 meV/atom. [11]

For comparison, the best Al-Co structure models [9] are ≈ 10 meV/atom above the tie-line. In typical decagonal approximants, the energy is reduced ~ 50 meV/atom after Al atoms are allowed to “pucker” out of the layers (doubling the c axis to 8\AA), and to organize the proper correlations between the puckerings of nearby atoms. We have not yet investigated puckering in the present system, which would require molecular-dynamics simulation followed by relaxation [4, 5].

We also attempted to make our structure more realistic by going to a ternary, having recognized that the internal sites in HBS tiles (besides the interior vertex) are always “problem sites” in Al-transition metal decagonals. (E.g., those are the atoms that “pucker” [5].) The root problem is that the two Al in one Boat are a bit overpacked, in view of the Al-Al hardcore distance. Could we fill these sites with (somewhat smaller) Cu atoms? No: when we tried an Al-Cu-Co ternary (with pair potentials), Cu atoms entered Hexagons forming CuCo pairs (as seen earlier in Ref. [7].)

IV. ACKNOWLEDGEMENTS

This work was supported by U.S. DOE grant DE-FG02-89ER-45405; M.M. was also supported by Slovak research grants VEGA 2/0157/08 and APVV-0413-06. We thank A. Bhagat for discussions. C.L.H. is grateful to the Slovak Academy of Sciences for hospitality.

-
- [1] Lim, S.; Mihalkovič, M.; Henley, C. L.: Penrose matching rule from realistic potentials. (Proc. “Quasicrystals Silver Jubilee” Tel Aviv 2007) Phil. Mag. 90 (2008), to appear.
 - [2] Penrose, R.: The role of aesthetics in pure and applied mathematical research. Bull. Inst. Math. Appl. 10 (1974) 266-271.
 - [3] Mihalkovič, M.; Al-Lehyani, I.; Cockayne, E.; Henley, C. L.; Moghadam, N.; Moriarty, J. A.; Wang, Y.; Widom, M.: Total-energy-based prediction of a quasicrystal structure” for decagonal Al-Ni-Co. Phys. Rev. B 65 (2002) 104205.
 - [4] Gu, N.; Mihalkovič, M.; Henley, C. L.: Energy-based Structure Prediction for $d(\text{Al}_{70}\text{Co}_{20}\text{Ni}_{10})$. Phil. Mag. Lett. 87 (2007) 923-933.
 - [5] Gu, N.; Henley, C. L.; Mihalkovič, M.: Co-rich decagonal Al-Co-Ni: predicting structure, orientational order, and puckering. Phil. Mag. 86 (2006) 593-599.
 - [6] Moriarty, J. A.; Widom, M.: First-principles interatomic potentials for transition-metal aluminides: theory and trends across the 3d series. Phys. Rev. B 56 (1997) 7905-7917.
 - [7] Cockayne, E.; Widom, M.: Ternary Model of an Al-Cu-Co Decagonal Quasicrystal. Phys. Rev. Lett. 81 (1998) 598-601.
 - [8] Kresse, G.; Hafner, J.: Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47 (1993) 558-561. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996), “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”.
 - [9] Mihalkovič, M.; Widom, M.: Cohesive energies in the Al-Co binary alloy system. Phys. Rev. B 75 (2007) 014207.
 - [10] With the internal Al removed but $r_{\text{cut}} = 7\text{\AA}$, the correct Fat-Fat rule is *still* upheld, presumably by Al(a)-Co interactions at $R \approx 6.5\text{\AA}$.
 - [11] After ab-initio relaxation, the cell expands by 1.20% and 1.85% along the long and short axes in-plane, and by 1.96% interlayer. The relatively small volume change supports the validity of the pair potentials [6], which were conditioned on a particular electron density.